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### (54) Heat conductive silicone composition and semiconductor device

(57) A heat conductive silicone composition comprising (A) an alkenyl group-bearing organopolysiloxane, (B) an organohydrogenpolysiloxane having Si-H groups on side chains, (C) an organohydrogenpolysiloxane having an Si-H group at either end, (D) a filler consisting of aluminum powder and zinc oxide powder

in a weight ratio of from 1/1 to 10/1, (E) a platinum catalyst, and (F) a regulator has a high thermal conductivity and maintains flexibility even when exposed to heat for an extended period of time.

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**Description**

[0001] This invention relates to silicone compositions having heat transfer ability, and semiconductor devices using the same.

**5**  
**BACKGROUND**

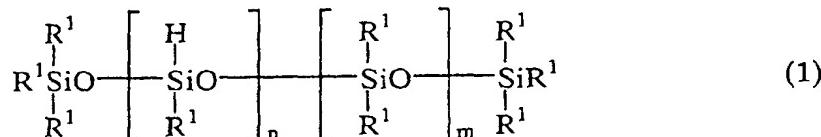
[0002] IC packages such as central processing units (CPU) and other electronic parts mounted on printed circuit boards will deteriorate their performance or even fail on account of temperature rises by the heat generated during operation. In the prior art, heat dissipating sheets or grease having a good heat transfer ability is employed between the IC package and the finned heat sink. The heat dissipating sheets have the advantage of easy mounting. Since the surface of CPU or finned heat sink is microscopically irregular despite apparent flatness, it is difficult in practice to intimately bond the heat dissipating sheet to the adherend surface, often leaving an air gap therebetween. This leads to the disadvantage that the heat dissipating sheet fails to exert the heat dissipating effect as desired. One typical solution proposed thus far is to provide the heat dissipating sheet with a pressure-sensitive adhesive layer for achieving a more intimate bond, which is still insufficient. The heat dissipating grease can intimately follow and contact the surface of CPU and finned heat sink independent of irregularities on the adherend surface, but can foul adjacent parts and gives rise to the problem of oil leakage during long-term service. To overcome these problems, JP-A 61-157569 and 8-208993 propose the use of liquid silicone rubber compositions as potting agent or adhesive. However, these silicone rubber compositions have a short thermal conductivity on account of the reduced content of heat conductive filler. Due to heat release from CPU and moisture in the ambient atmosphere, the silicone rubber compositions in the cured state tend to gradually harden, finally losing flexibility so that they peel off from the substrate or CPU. As a result, the compositions undesirably increase their thermal resistance with the lapse of time.

**25**  
[0003] In general, the aim of the invention is to provide heat conductive silicone compositions which combine thermal conductivity, preferably higher than in previous such compositions, with flexibility that is preferably maintained even when exposed to heat over a long period of time. Aspects to be protected include the uncured and cured compositions, articles and especially films of the cured composition, methods of making and using any of these, semiconductor or IC devices including them, and the manufacture of such devices.

**30**  
[0004] The invention is directed at a silicone composition of the addition reaction curing type comprising organopolysiloxane having at least two alkenyl groups in a molecule and organohydrogenpolysiloxane having at least two silicone atom-bonded hydrogen atoms per molecule. By using organohydrogenpolysiloxanes of the following general formulae (1) and (2) in combination, blending a mixture of aluminium powder and zinc oxide powder as a filler, and optionally, blending a long chain alkyl group-bearing organosilane of the following general formula (3), there is obtained a heat conductive silicone composition which has a good thermal conductivity by virtue of a possible increase in the amount of filler blended and maintains flexibility even when exposed to heat for a long period of time. Efficient heat dissipation is achieved by providing a cured film of the heat conductive silicone composition between a semiconductor chip and a heat dissipator. More specifically, in a heat dissipating means for IC package comprising an IC package mounted on a printed circuit board and a heat dissipator disposed on the surface of the IC package, the heat conductive silicone composition is cast between the IC package and the heat dissipator and heat cured thereat to form a cured film having a thickness of e.g. 10 to 100  $\mu\text{m}$ .

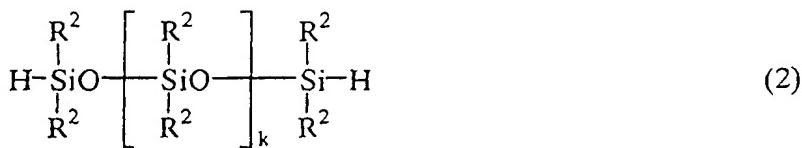
**40**  
[0005] Accordingly, one aspect herein is a heat conductive silicone composition comprising

- (A) 100 parts by weight of an organopolysiloxane containing at least two alkenyl groups in a molecule and having a viscosity of 10 to 100,000  $\text{mm}^2/\text{s}$  at 25°C,  
**45**  
(B) an organohydrogenpolysiloxane of the general formula (1):



**55**  
wherein R<sup>1</sup> is an alkyl group of 1 to 6 carbon atoms, n and m are positive numbers satisfying  $0.01 \leq n/(n+m) \leq 0.3$ ,

(C) an organohydrogenpolysiloxane of the general formula (2):



10 wherein  $\text{R}^2$  is an alkyl group of 1 to 6 carbon atoms, and  $k$  is a positive number of 5 to 1,000, components (B) and (C) being contained in such amounts that the ratio of the number of Si-H groups in components (B) and (C) combined to the number of alkenyl groups in component (A) is from 0.6/1 to 1.5/1, and in such a proportion that the ratio of the number of Si-H groups in component (C) to the number of Si-H groups in component (B) is from 1.0/1 to 10.0/1,

15 (D) 800 to 1,200 parts by weight of a filler consisting of aluminum powder having a mean particle size of 0.1 to 50  $\mu\text{m}$  and zinc oxide powder having a mean particle size of 0.1 to 5  $\mu\text{m}$  in a weight ratio of from 1/1 to 10/1,

15 (E) a catalyst selected from the group consisting of platinum and platinum compounds, e.g. in an amount as to give 0.1 to 500 ppm of elemental platinum based on the weight of component (A), and preferably also

(F) 0.01 to 1 part by weight of a regulator for suppressing the catalytic activity of component (E). The composition has a viscosity of 50 to 1,000 Pa·s at 25°C.

20 [0006] In a preferred embodiment, the composition further includes (G) 0.01 to 10 parts by weight of an organosilane of the general formula (3):



25 wherein  $\text{R}^3$  is an alkyl group of 6 to 15 carbon atoms,  $\text{R}^4$  is a monovalent hydrocarbon group of 1 to 8 carbon atoms,  $\text{R}^5$  is an alkyl group of 1 to 6 carbon atoms, "a" is an integer of 1 to 3, "b" is an integer of 0 to 2, and  $a+b$  is an integer of 1 to 3.

30 [0007] Also contemplated herein is a semiconductor device comprising an IC package mounted on a printed circuit board and a heat dissipator disposed on the surface of the IC package for dissipating heat from the IC package, a cured film of the heat conductive silicone composition defined above having a thickness of 10 to 100  $\mu\text{m}$  being interposed between the IC package and the heat dissipator. Other aspects are in the claims and/or mentioned below.

#### BRIEF DESCRIPTION OF THE DRAWINGS

35 [0008] The only figure, FIG. 1 is a schematic cross-sectional view of a semiconductor device according to one embodiment of the invention.

#### FURTHER EXPLANATIONS; OPTIONS AND PREFERENCES

40 [0009] Component (A) of the heat conductive silicone composition according to the invention is an organopolysiloxane having at least two alkenyl groups, each directly attached to a silicon atom, in a molecule. It may be either straight or branched while a mixture of two or more organopolysiloxanes having different viscosity is acceptable.

45 [0010] The organopolysiloxane used herein is preferably of the following average compositional formula (4).



50 Herein  $\text{R}^6$ , which may be the same or different, is a substituted or unsubstituted monovalent hydrocarbon group of 1 to 18 carbon atoms, preferably 1 to 3 carbon atoms, and  $c$  is a positive number in the range of 1.5 to 2.8, preferably 1.8 to 2.5, and more preferably 1.95 to 2.05.

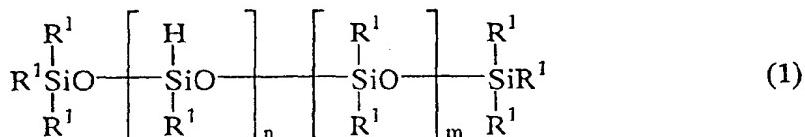
55 [0011] Examples of the substituted or unsubstituted monovalent hydrocarbon group attached to a silicon atom represented by  $\text{R}^6$  include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, cyclohexyl, octyl, nonyl, decyl and dodecyl; aryl groups such as phenyl, tolyl, xylyl and naphthyl; aralkyl groups such as benzyl, phenylethyl and 2-phenylpropyl; alkenyl groups such as vinyl, allyl, propenyl, isopropenyl, 1-but enyl, 1-hexenyl, cyclohexenyl and octenyl; and substituted ones of the foregoing groups in which some or all of the hydrogen atoms are substituted with halogen atoms (e.g., fluorine, bromine and chlorine), cyano groups or the like, such as

chloromethyl, chloropropyl, bromoethyl, 3,3,3-trifluoropropyl and cyanoethyl. It is preferred for ease of synthesis and economy that at least 90% of the R<sup>6</sup> groups be methyl.

[0012] At least two of the R<sup>6</sup> groups are alkenyl groups, preferably of 2 to 8 carbon atoms, especially 2 to 6 carbon atoms. It is preferred that the content of alkenyl groups be 0.001 to 20 mol%, especially 0.01 to 10 mol%, of the entire organic groups attached to silicon atoms, that is, the entire substituted or unsubstituted monovalent hydrocarbon groups represented by R<sup>6</sup> in formula (4). The alkenyl groups may be attached to the silicon atoms at the ends of the molecular chain or silicon atoms intermediate the molecular chain or both. From the standpoints of composition curing rate and cured physical properties and especially flexibility, the organopolysiloxane used herein should preferably have at least an alkenyl group attached to the silicon atom at the end of the molecular chain.

[0013] The organopolysiloxane (A) should have a viscosity at 25°C in the range of 10 to 100,000 mm<sup>2</sup>/s, preferably 100 to 50,000 mm<sup>2</sup>/s. With a viscosity of less than 10 mm<sup>2</sup>/s, the composition may become less stable in storage. With a viscosity of more than 100,000 mm<sup>2</sup>/s, the composition may become less castable.

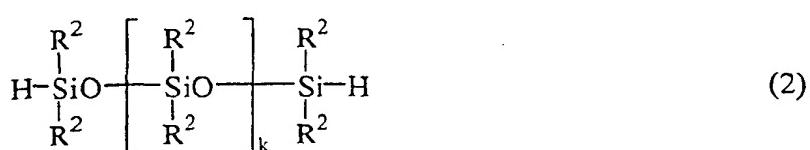
[0014] Component (B) is an organohydrogenpolysiloxane having at least two, preferably at least three, silicon atom-bonded hydrogen atoms (i.e., Si-H groups) in a molecule. Specifically, it is a linear organohydrogenpolysiloxane having Si-H groups on side chains, represented by the following general formula (1):



25 wherein R<sup>1</sup> is an alkyl group of 1 to 6 carbon atoms, and n and m are positive numbers satisfying 0.01 ≤ n/(n+m) ≤ 0.3.

[0015] More particularly, R<sup>1</sup> is an alkyl group selected from among methyl, ethyl, propyl, butyl, hexyl and analogues. Of these, methyl is preferred because of ease of synthesis and cost. If n/(n+m) in formula (1) is less than 0.01, the composition is prevented from crosslinking into a network structure. If n/(n+m) is more than 0.3, more Si-H groups are left unreacted after initial cure, so that moisture or other factors can drive crosslinking reaction to an excessive extent with the passage of time, resulting in the composition losing flexibility. For this reason, n/(n+m) in formula (1) should be in the range of 0.01 to 0.3, preferably 0.05 to 0.2. The sum of n+m is preferably about 5 to 500, especially about 10 to 300, though not limited thereto.

[0016] Component (C) is an organohydrogenpolysiloxane of the general formula (2).



40 [0017] Herein R<sup>2</sup> is an alkyl group of 1 to 6 carbon atoms, such as methyl, ethyl, propyl, butyl or hexyl as exemplified for R<sup>1</sup>. It is preferred for ease of synthesis and economy that at least 90% of the R<sup>2</sup> groups be methyl.

[0018] In formula (2), k is a positive number of 5 to 1,000, preferably 10 to 100. With k less than 5, the organohydrogenpolysiloxane tends to be volatile and is thus unsuited for electronic parts, whereas a k value in excess of 1,000 may lead to increased viscosity and difficulty to handle.

[0019] The amount of components (B) and (C) combined is such that the ratio of the number of Si-H groups in components (B) and (C) to the number of alkenyl groups in component (A) may range from 0.6/1 to 1.5/1, preferably from 0.7/1 to 1.4/1. If the ratio (number of Si-H groups in components B and C)/(number of alkenyl groups in component A) is less than 0.6, the composition may not form a satisfactory network structure or reach the necessary cured hardness. If the ratio is more than 1.5, unreacted Si-H groups can undergo excessive crosslinking reaction with moisture so that the composition loses flexibility. Components (B) and (C) are used in such a proportion that the ratio of the number of Si-H groups in component (C) to the number of Si-H groups in component (B) is from 1.0/1 to 10.0/1, preferably from 1.5/1 to 5.0/1. If the ratio (number of Si-H groups in component C)/(number of Si-H groups in component B) is less than 1.0, flexibility may not be adequate after curing. If the same ratio is more than 10.0, curing may be insufficient.

[0020] Component (D) is a filler for imparting thermal conductivity to the inventive composition. The filler used herein

is a mixture of aluminum powder and zinc oxide powder. If the aluminum powder has a mean particle size of less than 0.1 µm, the resulting composition may be rather viscous and less castable. If the aluminum powder has a mean particle size of more than 50 µm, the composition may become non-uniform. For this reason, the aluminum powder used herein should have a mean particle size of 0.1 to 50 µm, preferably 1 to 20 µm. If the zinc oxide powder has a mean particle size of less than 0.1 µm, the resulting composition may be rather viscous and less castable. If the zinc oxide powder has a mean particle size of more than 5 µm, the composition may become non-uniform. For this reason, the zinc oxide powder used herein should have a mean particle size of 0.1 to 5 µm, preferably 1 to 4 µm. The aluminum and zinc oxide powder particles may be of spherical or irregular shape.

[0021] The thermal conductivity of these minerals is discussed below. Aluminum and zinc oxide powders generally have a thermal conductivity of about 237 W/mK and about 20 W/mK, respectively, indicating that aluminum powder alone is more advantageous in achieving a higher thermal conductivity. However, aluminum powder used alone gives a composition which is unstable and prone to oil separation. It has been found that mixing aluminum powder with zinc oxide powder is effective for preventing oil separation. If the weight ratio of aluminum powder/zinc oxide powder is less than 1/1, the resulting composition becomes less heat conductive. If the same ratio is more than 10/1, noticeable oil separation occurs with time. Therefore, the weight ratio of aluminum powder/zinc oxide powder is from 1 to 10, preferably at least 2 but not more than 8.

[0022] The amount of the aluminum powder/zinc oxide powder mixture blended is 800 to 1,200 parts, preferably 850 to 1,150 parts by weight per 100 parts by weight of component (A). On this basis, the composition containing less than 800 parts of the powder mixture becomes less heat conductive whereas the composition containing more than 1,200 parts of the powder mixture becomes less castable.

[0023] Component (E) is a catalyst selected from among platinum and platinum compounds, which serves to promote addition reaction between alkenyl groups in component (A) and Si-H groups in components (B) and (C). Exemplary catalysts are elemental platinum, chloroplatinic acid, platinum-olefin complexes, platinum-alcohol complexes, and platinum coordinate compounds. An appropriate amount of the catalyst is usually to give 0.1 to 500 parts by weight of platinum atoms per million parts by weight of component (A). Less than 0.1 ppm of platinum may not exert catalytic effects. Usually, no further increase in curing rate is expectable with more than 500 ppm of platinum.

[0024] Component (F) is a regulator, preferred for restraining the progress of hydrosilylation reaction at room temperature for thereby extending the shelf life and pot life. The reaction regulator may be selected from well-known compounds, for example, acetylene compounds, nitrogen compounds, organic phosphorus compounds, oxime compounds and organic chlorine compounds. An appropriate amount of the regulator (F) is 0.01 to 1 part by weight per 100 parts by weight of component (A). Less than 0.01 part of the regulator may not significantly improve the shelf life or pot life whereas more than 1 part of the regulator may reduce curability. On use, the regulator may be diluted with an organic solvent such as toluene, xylene or isopropyl alcohol in order to improve its dispersion in the silicone resin.

[0025] In a preferred embodiment, the inventive composition further contains (G) an organosilane of the following general formula (3) to improve the wetting of the filler with the silicone components. The organosilane serves as a wetter.

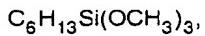


Herein R<sup>3</sup> is an alkyl group of 6 to 15 carbon atoms, R<sup>4</sup> is a monovalent hydrocarbon group of 1 to 8 carbon atoms, R<sup>5</sup> is an alkyl group of 1 to 6 carbon atoms, "a" is an integer of 1 to 3, "b" is an integer of 0 to 2, and the sum of a+b is an integer of 1 to 3.

[0026] Referring to formula (3), R<sup>3</sup> is an alkyl group of 6 to 15 carbon atoms, for example, hexyl, octyl, nonyl, decyl, dodecyl and tetradecyl. With less than 6 carbon atoms, the wettability to the filler is insufficient. With more than 15 carbon atoms, the organosilane becomes inconvenient to handle because of solidification at room temperature and the resulting composition has poor low-temperature properties. The letter "a" is 1, 2 or 3, preferably equal to 1. R<sup>4</sup> is selected from saturated or unsaturated monovalent hydrocarbon groups of 1 to 8 carbon atoms, for example, alkyl, cycloalkyl and alkenyl groups. Illustrative are alkyl groups such as methyl, ethyl, propyl, hexyl and octyl, cycloalkyl groups such as cyclopentyl and cyclohexyl, alkenyl groups such as vinyl and allyl, aryl groups such as phenyl and tolyl, aralkyl groups such as 2-phenylethyl and 2-methyl-2-phenylethyl, and halogenated hydrocarbon groups such as 3,3,3-trifluoropropyl, 2-(nanofluorobutyl)ethyl, 2-(heptadecafluoroctyl)ethyl and p-chlorophenyl. Methyl and ethyl are preferred among others. R<sup>5</sup> is an alkyl group of 1 to 6 carbon atoms, for example, methyl, ethyl, propyl, butyl, pentyl and hexyl, and mixtures thereof, with methyl and ethyl being preferred.

[0027] Illustrative, non-limiting, examples of the organosilane of the formula (3) include

55



5                   C<sub>10</sub>H<sub>21</sub>Si(OCH<sub>3</sub>)<sub>3</sub>,

10                  C<sub>12</sub>H<sub>25</sub>Si(OCH<sub>3</sub>)<sub>3</sub>,

15                  C<sub>12</sub>H<sub>25</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>,

20                  C<sub>10</sub>H<sub>21</sub>Si(CH<sub>3</sub>)(OCH<sub>3</sub>)<sub>2</sub>,

25                  C<sub>10</sub>H<sub>21</sub>Si(C<sub>6</sub>H<sub>5</sub>)(OCH<sub>3</sub>)<sub>2</sub>,

30                  C<sub>10</sub>H<sub>21</sub>Si(CH<sub>3</sub>)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>,

35                  C<sub>10</sub>H<sub>21</sub>Si(CH=CH<sub>2</sub>)(OCH<sub>3</sub>)<sub>2</sub>,

40                  and

45                  C<sub>10</sub>H<sub>21</sub>Si(CH<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub>)(OCH<sub>3</sub>)<sub>2</sub>.

**[0028]** An appropriate amount of the organosilane blended is 0.01 to 10 parts, preferably 0.1 to 7 parts by weight per 100 parts by weight of component (A). Less than 0.01 part of the organosilane exerts less wetting effects whereas more than 10 parts of the organosilane gives little further effects and is uneconomical.

**[0029]** In addition to the above-mentioned components (A) to (F) and optional component (G), the heat conductive silicone composition of the invention may have added thereto additives if desired. For example, there may be added adhesion aids for chemically bond and secure the IC package (such as CPU) to the heat dissipator (such as heat sink) and antioxidants for preventing deterioration.

**[0030]** The heat conductive silicone composition is obtainable by mixing the above-mentioned essential and, if desired, optional components. The composition in the one-part addition form allows for long-term, low-temperature storage.

**[0031]** In a typical advantageous application, the heat conductive silicone composition of the invention is interposed between a semiconductor chip and a heat dissipator so the composition serves as a heat transfer member for conducting the heat produced by the semiconductor chip to the heat dissipator. Where the composition is used as a heat transfer member or in another application, it is cured under appropriate conditions, for example, by heating at a temperature of about 60 to 200°C for about 5 to 120 minutes.

**[0032]** According to the invention, a semiconductor device is provided wherein a cured film of the heat conductive silicone composition is interposed between a semiconductor chip and a heat dissipator. In a specific embodiment of the invention, there is provided a heat dissipating apparatus for IC package comprising an IC package mounted on a printed circuit board and a heat dissipator disposed on the surface of the IC package for dissipating heat from the IC package wherein a cured film of the heat conductive silicone composition is interposed between the IC package and the heat dissipator.

**[0033]** In fabricating the semiconductor devices according to the invention, the heat conductive silicone composition is contained in a syringe, which may be conventional, and dispensed therefrom onto the surface of IC packages such as CPU. For such application, the composition should preferably have a viscosity in the range of 50 to 1,000 Pa·s, more preferably 100 to 400 Pa·s at 25°C. A composition with a viscosity of less than 50 Pa·s may drip upon application whereas a viscosity of higher than 1,000 Pa·s may impede efficient application.

**[0034]** By applying the heat conductive silicone composition between a printed circuit board and a heat dissipator and fastening the board and the heat dissipator together by means of a clamp or the like, the composition is secured and compressed between the IC package and the heat dissipator. The composition interposed between the IC package and the heat dissipator preferably has a thickness in the range of 10 to 100 µm, preferably 25 to 50 µm. A thickness of less than 10 µm allows a slight shift of compression to create a gap between the IC package and the heat dissipator whereas a thickness of more than 100 µm provides a substantial thermal resistance which may be unacceptable in

some cases of heat dissipation.

[0035] After dispensing, the composition cures with the heat produced by the IC package. Once cured, the composition has a sufficient tack to prevent displacement and a long-lasting flexibility to prevent its peeling from the substrates. Alternatively, the composition may be positively heat cured after dispensing.

5 [0036] According to the invention, in a heat dissipating apparatus for IC package comprising an IC package mounted on a printed circuit board and a heat dissipator in pressure contact with the surface of the IC package, the heat conductive silicone composition is interposed between the IC package and the heat dissipator.

10 [0037] In this embodiment, the heat conductive silicone composition interposed between the IC package and the heat dissipator is pasty and castable, so that even when the IC package and the heat dissipator have irregularities on their surface, the gaps therebetween can be evenly filled with the silicone composition simply by pressing the heat dissipator onto the silicone composition on the IC package. By virtue of the heat produced by the IC package, the silicone composition is cured and bonded in situ. The silicone composition does not lose flexibility with time or peel from the substrates. Therefore, the silicone composition ensures to exert the desired heat dissipating effects, improving the reliability of the overall electronic part.

15

#### EXAMPLE

[0038] Examples of the invention are given below by way of illustration and not by way of limitation.

20 Examples & Comparative Examples

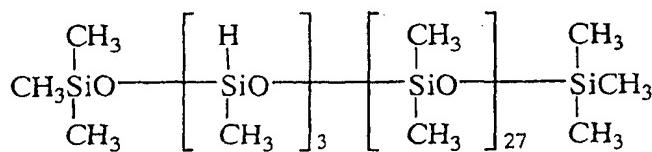
[0039] The following components were furnished. Component (A)

25 A-1: dimethylpolysiloxane blocked with a dimethylvinylsilyl group at either end and having a viscosity of 600 mm<sup>2</sup>/s at 25°C

Component (B) Organohydrogenpolysiloxanes B-1 to B-4 were used.

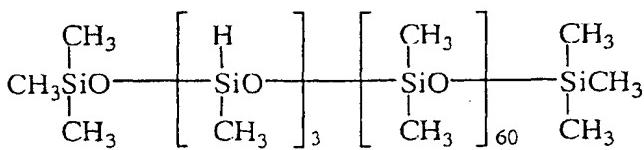
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B-1

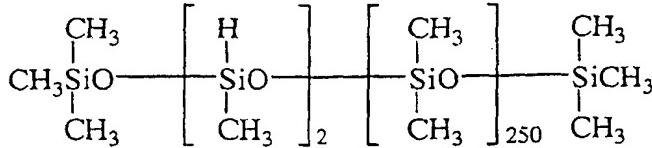


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B-2



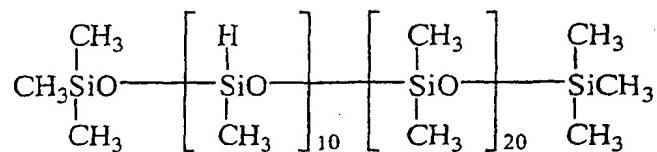
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B-3  
(Comparison)

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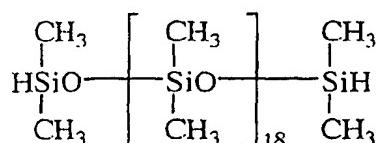
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5                   B-4  
   (Comparison)

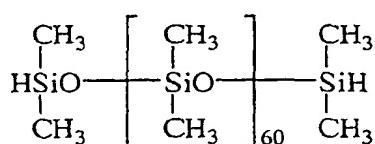


10                  Component (C) Organohydrogenpolysiloxanes C-1 and C-2 were used.

15                  C-1



20                  C-2



25                  Component (D)

Powder mixtures D-1 to D-6 were obtained by mixing aluminum powder and zinc oxide powder in a weight ratio as shown in Table 1 at room temperature for 15 minutes in a 5-liter planetary mixer (Inoue Mfg. K.K.).

30                  Aluminum powder with a mean particle size of 4.9  $\mu\text{m}$

Aluminum powder with a mean particle size of 15.0  $\mu\text{m}$

Zinc oxide powder with a mean particle size of 1.0  $\mu\text{m}$

35                  Table 1

Component (D)	4.9 $\mu\text{m}$ Al powder (g)	15.0 $\mu\text{m}$ Al powder (g)	1.0 $\mu\text{m}$ ZnO powder (g)	Mixing ratio (Al powder/ZnO powder)
D-1	2000	0	1000	2
D-2	2500	0	500	5
D-3	0	2500	500	5
D-4	2667	0	333	8
D-5 (comparison)	143	0	2857	0.5
D-6 (Comparison)	2750	0	250	11

50                  Component (E) E-1: A-1 solution of platinum-divinyltetramethyl-disiloxane complex, containing 1% of platinum atoms

Component (F) F-1: 50% toluene solution of 1-ethynyl-1-cyclohexanol

55                  Component (G) Organosilanes G-1 and G-2 were used. G-1:  $\text{C}_6\text{H}_{13}\text{Si}(\text{OCH}_3)_3$  G-2:  $\text{C}_{10}\text{H}_{21}\text{Si}(\text{OCH}_3)_3$

[0040] Heat conductive silicone compositions of Examples 1-6 and Comparative Examples 1-10 were prepared by mixing components (A) to (F) as follows. In a 5-liter planetary mixer (Inoue Mfg. K.K.), component (A) was placed,

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component (D) was added thereto in the amount shown in Table 2 or 3, component (G) was optionally added, and the contents were mixed for one hour at 70°C. The mixture was cooled down to room temperature, to which components (B), (C), (E) and (F) were added thereto in the amounts shown in Table 2 or 3, and the contents were mixed until uniform. [0041] The compositions thus obtained were examined by the following tests. The results are shown in Tables 2 and 3.

5

(1) Viscosity:

measured by a rotary viscometer at 25°C

10 (2) Thermal conductivity Each composition was cast into a mold of 3 cm deep and covered with a kitchen wrap. A thermal conductivity was measured by a quick thermal conductivity meter Model QTM-500 (Kyoto Electronic Industry K.K.).

(3) Shelf stability

After each composition was held at -5°C for one month, its outer appearance was visually inspected.

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O: no separation

X: noticeable oil bleeding

(4) Hardness

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[0042] The composition was evaluated for flexibility with time by measuring the hardness thereof using an Asker C hardness meter (low hardness scale) by Kobunshi Keiki K.K. Each composition was cast into a mold of 10 mm deep and heated at 125°C for one hour, forming a rubber sheet of 10 mm thick, which was cooled down to 25°C. The initial hardness of the rubber sheet was measured. Thereafter, the rubber sheet was held for 100 hours in an atmosphere having a temperature of 130°C, a humidity of 100% and a pressure of 2 atm. It was cooled down to 25°C and measured for hardness again (aged hardness).

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Table 2

Component (pbw)	Example					
	1	2	3	4	5	6
A-1	100	100	100	100	100	100
B-1	4.6		3.5		1.6	3.3
B-2		9.6		7.2		
B-3						
B-4						
C-1	6.6	6.6	7.7		6.2	12.3
C-2				24		
Si-H/Si-Vi (number ratio)	1.0	1.0	1.0	1.0	0.7	1.4
(number of Si-H in C)/ (number of Si-H in B)	1.5	1.5	2.3	2.3	4.0	4.0
D-1	900				850	1150
D-2		900				
D-3			900			
D-4				900		
D-5						
D-6						
G-1			6			
G-2				6		6
E-1	0.15	0.15	0.15	0.15	0.15	0.15

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Table 2 (continued)

	Component (pbw)	Example					
		1	2	3	4	5	6
5	F-1	0.45	0.45	0.45	0.45	0.45	0.45
	Viscosity (Pa-s)	210	190	175	139	180	315
10	Thermal conductivity (W/mK)	3.4	3.3	3.6	3.1	3.6	3.8
	Initial hardness (Asker C)	12	11	11	10	9	10
	Aged hardness*	12	12	11	10	9	12
	Shelf stability	○	○	○	○	○	○

\* 130°C/100% humidity/2 atm./100 hr.

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Table 3

Component	Comparative Example									
	1	2	3	4	5	6	7	8	9	10
(pbw)										
A-1	100	100	100	100	100	100	100	100	100	100
B-1	2.3	7.5	7.8	1.0						
B-2										
B-3					56.3					
B-4						1.3				
C-1	3.3	10.6	3.7	10.1	6.6	6.6	6.6	6.6	6.6	6.6
C-2										
Si-H/Si-VI (number ratio)	0.5	1.6	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
(number of Si-H in C)/(number of Si-H in B)	1.5	1.5	0.5	11	1.5	1.5	1.5	1.5	1.5	0
D-1	900				900	900	700	1300		900
D-2		900								
D-3			900							
D-4				900						
D-5									900	
D-6										900
G-1										
G-2										
E-1	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
F-1	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Viscosity (Pa·s)	250	171	220	219	80	231	110	not pasty	258	>1000
Thermal conductivity (W/mK)	3.4	3.2	3.4	3.4	1.7	3.7	2.2	-	1.9	3.5
Initial hardness (Asker C)	not cured	11	35	not cured	43	12	-	11	12	beyond the measurement limit

Table 3 (continued)

Component (pbw)	Comparative Example									
	1	2	3	4	5	6	7	8	9	10
Aged hardness*	-	41	50	-	-	51	12	-	12	12
Shelf stability	O	O	O	O	O	O	-	O	X	O

\*130°C/100% humidity/2 atm./100 hr.

[0043] Next, the heat conductive silicone compositions of the foregoing Examples were applied to semiconductor devices. FIG. 1 is an elevational cross section of a semiconductor device having an IC package according to one embodiment of the invention.

[0044] As shown in FIG. 1, the semiconductor device includes a CPU 2 mounted on a printed circuit board 3, a heat sink 4 disposed on the CPU 2, and a cured film 1 of the heat conductive silicone composition interposed between the CPU 2 and the heat sink 4. The heat sink 4 is formed of aluminum and provided with fins for increasing the surface area for enhancing heat dissipating effects. The printed circuit board 3 and the heat sink 4 are fastened and secured by a clamp 5, whereby the film 1 is compressed therebetween.

[0045] In this semiconductor device, 0.2 g of the heat conductive silicone composition of each Example was applied onto a surface area of 2 cm × 2 cm and interposed between the CPU 2 and the heat sink 4. The cured film of the silicone composition was 30 µm thick.

[0046] The IC package heat dissipating structure of the above-described arrangement was applied to CPU's having a heating temperature of the order of 150°C as commonly used in host computers and personal computers. Stable heat dissipation and diffusion took place, preventing the CPU's from performance deterioration or failure by heat accumulation.

[0047] Thus, it is possible to make a heat conductive silicone composition which has a high thermal conductivity and does not lose flexibility even when exposed to heat for a long time.

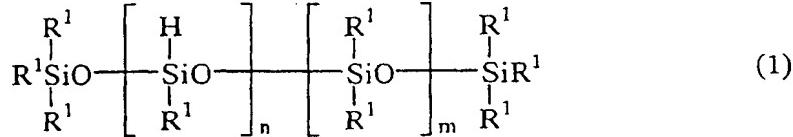
[0048] The disclosure of Japanese Patent Application No. 2001-133895 (the present priority application) is incorporated herein by reference.

[0049] Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described in the examples.

## 25 Claims

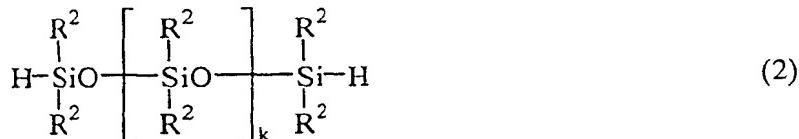
### 1. A heat conductive silicone composition comprising

(A) 100 parts by weight of organopolysiloxane containing at least two alkenyl groups in a molecule and having a viscosity of 10 to 100,000 mm<sup>2</sup>/s at 25°C,  
(B) organohydrogenpolysiloxane of the general formula (1):



40 wherein R<sup>1</sup> is an alkyl group of 1 to 6 carbon atoms, n and m are positive numbers satisfying 0.01 ≤ n/(n+m) ≤ 0.3,

(C) organohydrogenpolysiloxane of the general formula (2):



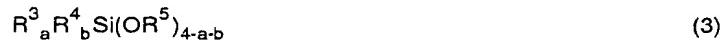
50 wherein R<sup>2</sup> is an alkyl group of 1 to 6 carbon atoms, and k is a positive number of 5 to 1,000, components (B) and (C) being contained in such amounts that the ratio of the total number of Si-H groups in components (B) and (C) to the number of alkenyl groups in component (A) is from 0.6/1 to 1.5/1, and in such a proportion that the ratio of the number of Si-H groups in component (C) to the number of Si-H groups in component (B) is from 1.0/1 to 10.0/1,

(D) 800 to 1,200 parts by weight in total of aluminum powder having a mean particle size of 0.1 to 50 µm and zinc oxide powder filler having a mean particle size of 0.1 to 5µm, said powders being in a weight ratio of from 1/1 to 10/1,

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(E) curing catalyst selected from platinum and platinum compounds, and  
(F) 0.01 to 1 part by weight of a regulator for suppressing the catalytic activity of component (E), said composition having a viscosity of 50 to 1,000 Pa·s at 25°C.

- 5      2. The composition of claim 1, further comprising (G) 0.01 to 10 parts by weight of organosilane of the general formula (3):



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wherein  $R^3$  is alkyl group of 6 to 15 carbon atoms,  $R^4$  is monovalent hydrocarbon group of 1 to 8 carbon atoms,  $R^5$  is alkyl group of 1 to 6 carbon atoms, "a" is an integer of 1 to 3, "b" is an integer of 0 to 2, and  $a+b$  is an integer of 1 to 3.

- 15     3. A semiconductor device comprising an IC package mounted on a printed circuit board and a heat dissipator disposed on the surface of the IC package for dissipating heat from the IC package, with a cured film of a heat conductive silicone composition of claim 1 or 2 having a thickness of 10 to 100 µm between the IC package and the heat dissipator.  
20     4. A method of manufacturing a device according to claim 3, in which the composition is applied and cured between the IC package and the heat dissipater.  
5. An article or film of a cured composition according to claim 1 or claim 2.

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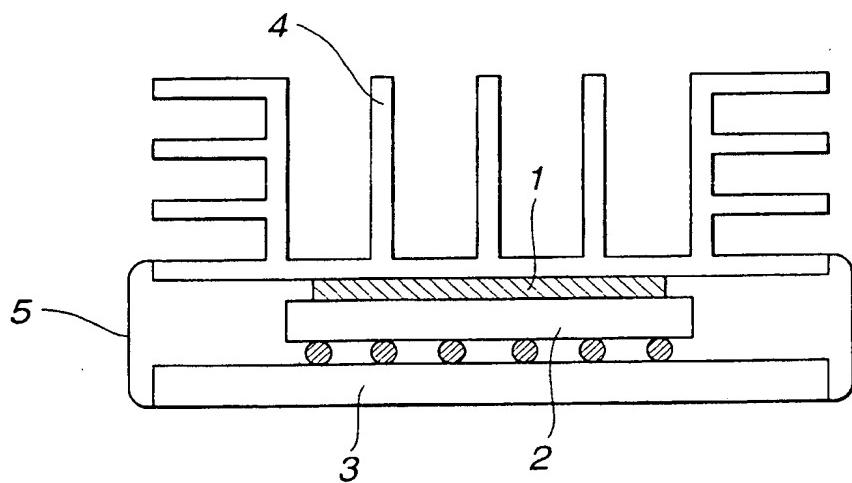
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**FIG.1**





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 02 25 3010

DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages		
A	US 6 069 201 A (KASHIWAGI TSUTOMU ET AL) 30 May 2000 (2000-05-30) * column 1, line 7 - line 11 * * column 2, line 27 - line 32 * * column 5, line 17 - line 28 * * column 9, line 53 - line 60 * * column 10, line 16 - line 20 * * column 15, line 18 - line 29; example 5 * * column 17, line 36 - line 40; example 8; table 3 *	1-5	C08L83/04 C08K3/08 C08K3/22 H01L23/373
A	US 4 845 164 A (GUTEK BETH I) 4 July 1989 (1989-07-04) * column 4, line 38 - line 64 * * column 7, line 5 - line 32 * * column 7, line 53 - line 55 * * column 9, line 63 - column 10, line 9; example 1 *	1	
A	EP 0 982 392 A (SHINETSU CHEMICAL CO) 1 March 2000 (2000-03-01) * page 14; example 4; table 2 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7)  C08L C08K H01L
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	13 August 2002	Öhm, M	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons S : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
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13-08-2002

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

